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NUCLEAR MAGNETIC DOUBLE RESONANCE EXPERIMENTS ON π-ALLYLPALLADIUM COMPLEXES

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SUMMARY

Exchange reactions of π-allylpalladium complexes have been studied by means of nuclear magnetic double resonance as developed by Forsên and Hoffman. Two examples are treated in this paper; (*a*) a simple left–right interchange in an asymmetric π-methallyl system containing four different protons, and (*b*) a π–σ rearrangement in symmetric dimeric π-allylpalladium compounds, too slow to be observed with line-broadening measurements. The accuracy of the rates obtained is rather limited, but the method offers an excellent opportunity of determining the reaction path in many-site problems.

INTRODUCTION

Nuclear magnetic resonance spectroscopy is extensively used for studying reaction rates in organic, inorganic and organometallic chemistry. The usual procedure is to deduce the chemical lifetimes involved from the line shapes in the NMR spectra[1]. Very fast reactions with rate constants up to 10^6 sec^{-1} can be studied when paramagnetic species are involved. However, processes with rate constants smaller than 1 sec^{-1} are difficult to investigate with line shape techniques. In a series of papers[2-5] Forsên and Hoffman have described an elegant method using nuclear magnetic double resonance (NMDR) for the study of exchange rates in systems with even considerably longer lifetimes. According to their procedure one of the exchanging protons is saturated with a second oscillator (double resonance) while the decay of the intensity of another exchanging proton to a new equilibrium value is followed. For NMDR experiments chemical lifetimes must be of the order of magnitude of spin–lattice relaxation times. The method also permits determination of the exchange path in many-site systems where simultaneous broadening of many signals occurs.

The number of applications has been very limited. Sometimes NMDR in exchanging systems is used as a method of indirect saturation[6], but applications in kinetic studies are rare[1 2]. However, NMDR may be very useful for the study of kinetics in organometallic chemistry and organic chemistry. It seemed worthwhile, therefore, to report a few examples of studies of organometallic molecules by means of NMDR. First the principles of the method are outlined following Forsên and Hoffman[2-5] (for an extensive treatment the reader is referred to their work). Also, several limitations of the technique are mentioned.

Homonuclear double resonance and chemical exchange

We consider a system with two exchanging non-equivalent spins A and B which have chemical lifetimes sufficiently long to give separate signals. In the absence of saturation effects the McConnell equation[2,7] for the longitudinal magnetization of spin A is

$$\frac{\mathrm{d}M_z^A}{\mathrm{d}t} = \frac{M_0^A - M_z^A}{T_{1A}} - \frac{M_z^A}{\tau_A} + \frac{M_z^B}{\tau_B} \tag{1}$$

where M_0^A is the equilibrium z magnetization, T_{1A} is the spin–lattice relaxation time and τ is the lifetime in the site indicated. In one of the experiments by Forsén and Hoffman the magnetization of the spins in site B is destroyed by strong irradiation, while the resonance of the spins in A is investigated with a weak rf field. If slow-passage conditions are assumed in A and a zero magnetization in B, the time dependence of the z magnetization M_z^A is given by

$$\frac{\mathrm{d}M_z^A}{\mathrm{d}t} = \frac{M_0^A}{T_{1A}} - \frac{M_z^A}{\tau_{1A}} \tag{2}$$

where $1/\tau_{1A} = 1/\tau_A + 1/T_{1A}$, *i.e.* the effective lifetime in the spin levels. After instantaneous saturation of B the decay of M_z^A is given by

$$M_z^A = M_0^A \cdot \frac{\tau_{1A}}{T_{1A}} + M_0^A \cdot \frac{\tau_{1A}}{\tau_A} \exp\left(-\frac{t}{\tau_{1A}}\right) \tag{3}$$

The equilibrium value of M_z^A is

$$M_z^A(t \rightarrow \infty) = M_0^A \cdot \frac{\tau_{1A}}{T_{1A}} \tag{4}$$

It is seen that a simple relation exists between the observed magnetization, the chemical lifetime and the spin–lattice relaxation time.

After removal of the irradiation of B the recovery of signal A is a function of τ_A, τ_B, T_{1B} and T_{1A}. The general equations for signal decays in many-site problems can be found in the original literature. We would only mention here—in a quantitative sense—that in a three-site system with an exchange mechanism (5)

$$\mathrm{B} \rightleftarrows \mathrm{A} \rightleftarrows \mathrm{C} \tag{5}$$

where B is irradiated to saturation, the relative demagnetization of $C(M_{zc}/M_{0c})$ is equal to or smaller than that of A.

The intensity of the signals as given above only contains the Boltzmann population, *i.e.* in terms of spin-density matrix notation it only involves the diagonal elements. A more precise expression of line shapes and signal intensity can be given with the aid of the density matrix method.

Obviously, relaxations of protons in sites A and B should be independent, as implied by McConnell's equations. When a perturbation of the Boltzmann population of one of the nuclei interferes with the population of another nucleus through the Overhauser effect[8], the relaxations are not independent and formula (3) cannot be applied. In regions where T_{1A} is large, the occurrence of a nuclear Overhauser effect is not fictitious. The relaxations are certainly independent when the main source of relaxation lies in the presence of traces of paramagnetic species (*e.g.* oxygen). Unfortunately, relaxation times are rather short under these conditions, which detracts from the attractiveness of the method: its capability of measuring chemical lifetimes several times longer than the relaxation times (under suitable conditions τ may reach 100 sec).

Whereas the restriction of independent relaxation times concerns both intra- and intermolecular reactions, the following only applies to systems with intramolecular (A, B) exchange. In this system no J_{AB}-coupling should occur, otherwise several errors may easily be made. The unsuspecting chemist might like to restrict himself to the measurement of peak heights. In these cases "enhancements" (after turning on the saturating field) will often be due to unresolved multiplets. Integration of the peaks versus a standard may yield slightly more accurate information, but very precise data (including signal decays) cannot be obtained by NMR integration. Apart from prohibiting peak-height measurement, spin–spin coupling can give rise to coupled (scalar) relaxation. This Overhauser effect cannot be distinguished from chemical exchange, since phenomenologically scalar relaxation and chemical exchange in partly saturated systems are the same.

EXPERIMENTAL

The NMDR experiments were conducted on the Varian spectrometers DP-60 and HA-100. The technique used on the DP-60 was similar to that described in literature[2-5]. Mostly the HA-100 model was preferred because of its great stability and better signal-to-noise ratio. In operation according to the "frequency-sweep mode" the appropriate signal can be continuously irradiated to saturation (H_2). The apparatus is used in the "lock-in" mode on some reference signal (tetramethylsilane). Since drift is negligible, the sweeping field (H_1) might be set at the resonance frequency[6] at the top of the line, whereas on the DP-60 instrument the linear sweep is used. H_1 must be kept very small to avoid saturation. We found that extremely small shifts (such as Bloch–Siegert shifts) already lead to a drop of the pen from the top of signal, in particular when sharp lines were being studied. Therefore we preferred a repetitive scan through the signal being followed. For this purpose we mounted a motor-driven potentiometer in series with the resistance of the HA-100 recorder determining H_1. The spectrum was recorded on an external recorder.

The audio-oscillator (HP Model 200 AB) could be set at about 30 Hz up or downfield from the chosen resonance frequency. The oscillator remained on while the spectra were taken. The frequency (H_2) was switched instantaneously to the appropriate frequency maintaining the same amplitude. This serves a two-fold purpose: it diminishes the Bloch–Siegert shift and it anticipates an undesirable drop of intensity due to electronic pick-up and changes in power distribution when H_2 is turned on in the usual manner. With these two modifications the results were reproducible within five percent.

RESULTS

The behaviour of π-methallylpalladium complexes has been extensively studied in this laboratory[8,10] by means of proton magnetic resonance. It has been found that the four protons of the methallyl group (absorbing at distinct frequencies in asymmetric compounds) under certain conditions become equivalent in the NMR spectrum. The processes responsible are determined by the anions, and donor and acceptor molecules present. The general formula of an asymmetric complex is $(\pi\text{-}C_4H_7)PdX(L)$, where $X = Cl^-$ or OAc^- and L = stibine, arsine or phosphine. When an excess ligand is present, a fast left–right interchange of the methallyl group is observed which results

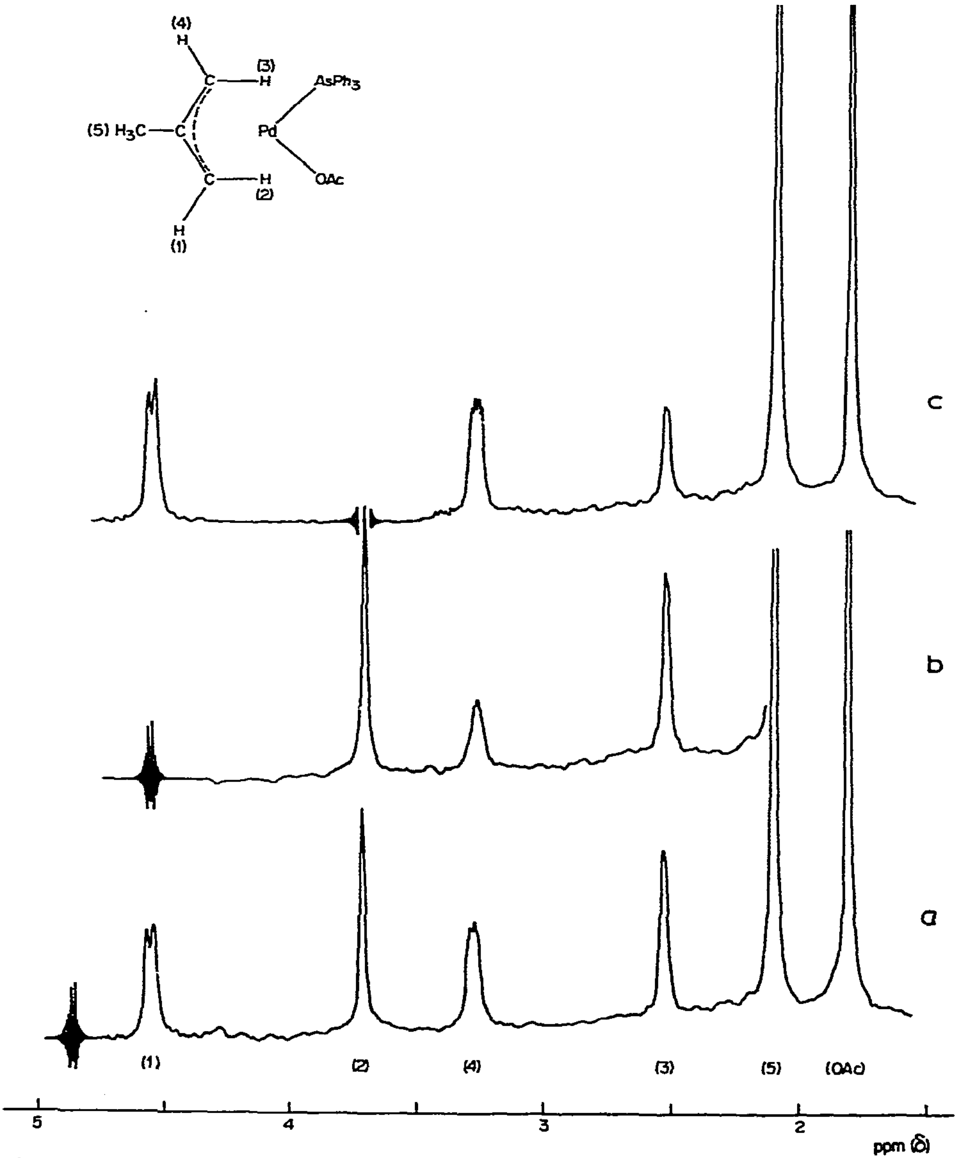


Fig. 1. NMDR spectra of $(\pi\text{-}C_4H_7)Pd(OAc)(AsPh_3)$ in $CDCl_3$ taken in frequency sweep-mode locked on TMS. a. Audiofield H_2 set 25 Hz above the resonance frequency of H(1). b. Audiofield H_2 set on the resonance frequency of H(1). c. Audiofield H_2 set on the resonance frequency of H(2). Irradiation of H(4) and H(3) yields similar pictures.

in two signals of the allyl group being symmetric within NMR limits. This reaction was called π-rotation[9]. From the chemical shifts of the slow-exchange spectrum and fast-exchange spectrum it has been deduced that protons (1) and (4) change places and so do protons (2) and (3). (The numbers and formula are given in Fig. 1.) The π-rotation is usually found in arsine complexes and is ascribed to ligand exchange. Free ligand is formed by dissociation.

The π-rotation of $(\pi\text{-}C_4H_7)Pd(OAc)(AsPh_3)$(left–right interchange) provides a simple example of NMDR applied to chemical exchange. The spectrum at $-30°$ is shown in Fig. 1a. The signals 1–4 broaden simultaneously at higher temperatures. If assignments of the peaks[9] are known, the NMDR experiments will show which interchanges are taking place. In the experiment yielding spectrum 1a the audio-oscillator was set about 25 Hz above the absorption frequency of proton (1) (see experimental). Fig. 1b shows the situation when H_2 saturated proton (1). It is seen that signals (2) and (3) are slightly higher when proton (1) is irradiated as a result of the removal of small couplings. The intensity of signal (4) is considerably decreased. Note that the peak height is still relatively large as a result of the decoupling $\{J[H(1)\text{–}H(4)] = 2.5$ Hz$\}$. For detailed studies integration of the signals would be necessary. In experiment 1c proton (2) was saturated by direct irradiation; we observe a marked decrease of the intensity of signal (3), whereas (1) and (4) are almost completely unaffected.

Hence the result is:

(*i*) irradiation of (1) yields partial saturation of (4), other intensities unaffected;

(*ii*) irradiation of (2) yields partial saturation of (3) and the reverse, other intensities unaffected.

This gives straightforward evidence of the reaction path, a left–right interchange. The restrictions to be made are that all nuclei have about the same longitudinal relaxation time and that the relaxation processes are independent. Relaxation times are about one second. They are rather short in spite of the precautions taken and we think that in these acetate complexes the main source for relaxation is the presence of paramagnetic traces. Hence the condition for independent relaxation is fulfilled. The rate of π-rotation is approximately 1 sec^{-1}, which can hardly be measured with line-broadening techniques.

The results of the second experiment are represented in Fig. 2. Three absorptions are found in the spectrum of $[(\pi\text{-methallyl})PdCl]_2$, which are assigned to the methyl group, and the *syn* (1)(4) and *anti* (2)(3) protons. Most of the π-allyl compounds show an isomerization of the *syn* and *anti* protons in the NMR spectrum[9]. The dimer $[(\pi\text{-}C_4H_7)PdCl]_2$, however, exhibits no broadening of the signals below 100°. Even the small couplings $[J(CH_3\text{–}H_{syn}) = 0.50$ Hz, $J(H_{syn}\text{–}H_{anti}) = 0.45$ Hz$]$ remain perceptible. Above 90° considerable decomposition occurs, and measurements below these temperatures are preferable. NMDR measurements performed at several temperatures clearly show that chemical exchange takes place. On account of the small coupling the signal height of the *anti* protons increases when the *syn* protons are irradiated (and the reverse) at temperatures below 60°. Integration of the signal indicated that a small enhancement of the total intensity also occurred when highly purified samples were used. The peak height of the protons observed in the NMDR spectrum decreased with increasing temperature. This can be ascribed to chemical exchange of the *syn* and *anti* protons, if it is assumed that no scalar relaxation occurs and that the total intensity of the signal has only slightly increased as a result of a dipole–dipole

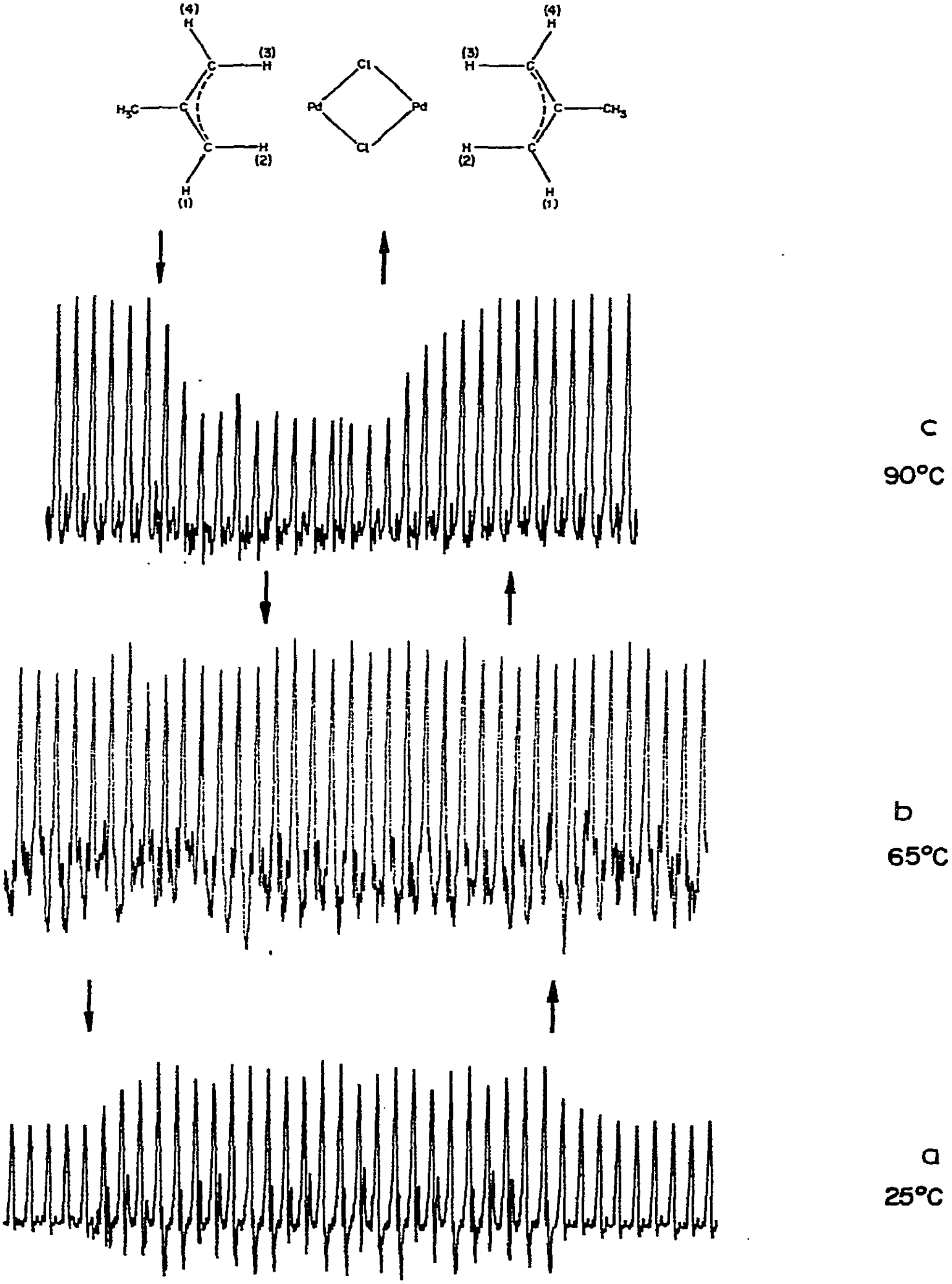


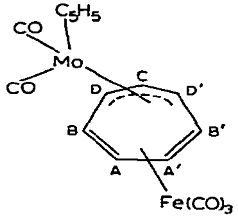
Fig. 2. Chemical exchange of *syn* and *anti* protons of π-methallylpalladium chloride dimer as shown by NMDR after irradiation of the *syn* protons. a. Increase of the signal of the *anti* proton owing to decoupling: no demagnetization at 25°. b. Slight demagnetization at 65° owing to chemical exchange. c. Increasing demagnetization at 90°. (Arrows indicate where a strong H_2 field was set at the resonance frequency and where it was offset about 30 Hz).

relaxation as observed at lower temperatures. At 90° the rate is of the order of magnitude of 0.2 sec^{-1}. The longitudinal relaxation time of all protons amounted to about 10 sec.

CONCLUSIONS

The accuracy of the rates obtained with NMDR is rather limited, but the same holds for those obtained from line-width measurements. The temperature range that can be covered with the two techniques together is wide and this enables us to determine the activation energy of the reaction with a much greater accuracy.

The NMDR technique is of particular interest in many-site systems. The case treated here, a left–right interchange in asymmetric π-allyl compounds, is relatively simple, but in several cases the number of possible reaction paths is larger. In a recent article Cotton and Reich[11] reported the fluxional behaviour of the cycloheptatrienyl ring in $(C_5H_5)(CO_2)Mo(C_7H_7)Fe(CO)_3$ with the postulated structure



Simultaneous broadening of the four NMR signals was observed and line-shape simulations led to the tentative conclusion that 1,2 shifts dominated. We suggest that NMDR, used together with T_1 measurements, would be an excellent tool for studying reactions of this kind.

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